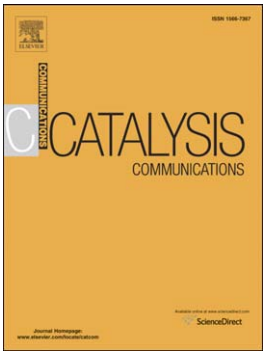

Hydroxyl group effect in novel NNN type pyridine based ruthenium (II) complex for the transfer hydrogenation of ketones

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Hydroxyl Group Effect in Novel NNN Type Pyridine Based Ruthenium (II) Complex for the Transfer Hydrogenation of Ketones

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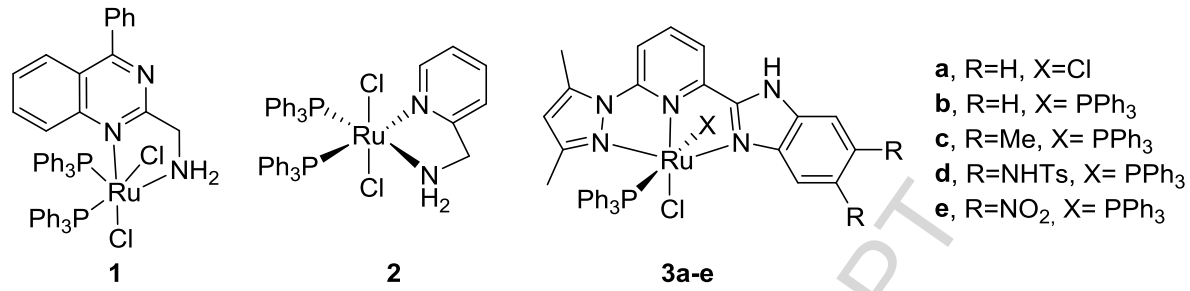
Abstract

The new NNN type pyridine ligands were prepared by using low cost and readily available starting materials and metalated with $RuCl_2(PPh_3)_3$ to obtain ruthenium(II) complexes. All structures were illuminated by NMR, HRMS, and FT-IR spectroscopy. The complexes exhibited good catalytic activity in transfer hydrogen reaction of ketones and it was found that a hydroxyl group on β-position of the pyridine ring had a dramatic effect on the catalyst efficiency.

Keywords: Transfer hydrogenation, substituent effect, ruthenium, NNN ligand, imino pyridine

Introduction

The design of efficient transition-metal catalysts plays a key role in achieving high productivity and selectivity in many catalytic reactions. Among the various catalytic reactions, transfer hydrogenation reactions (TH) have attracted a great deal of attention.[1] Complexes derived from ligands containing nitrogen donor atoms have been extensively studied and they were reported to exhibit high reactivity in TH [2-8]. Particularly, ruthenium based complexes coordinated with NNN,[9-12] NN,[13, 14] NO,[13] CNN [15-17] type ligands have been frequently applied as catalysts. Clearly, Noyori's Ru-ethylenediamine system is stated to be one of the most significant preliminary report in this area.[18, 19] Inspired from these systems, a variety of catalysts possessing heteroatoms with ligands such as quinazoline,[13, 20] pyridine,[21] imidazoyl,[10] etc. have been developed. Despite the fact that quinazoline **1** based ruthenium complex gave only 400 h^{-1} TOF values, its pyridine counterparts **2** were reported to have a TOF value of 2400 h^{-1} under similar reaction conditions.[5, 13] Yu and coworkers reported that ruthenium complexes coordinated with heterocyclic compounds bearing both pyridine and imidazoyl moiety **3a** gave high TOF values up to 705600 h^{-1} in TH reaction.[6] They also investigated the substituent effects of the electron-donating or electron-withdrawing functional groups on the imidazoyl moiety of the complex **3b-e** in catalytic activity studies and found that the stronger electron donating groups onto the coordinative imidazolyl arm of the NNN ligands were the higher the catalytic activities, which is presented in the following order 3d > 3c > 3b > 3e. (Scheme 1).[22]

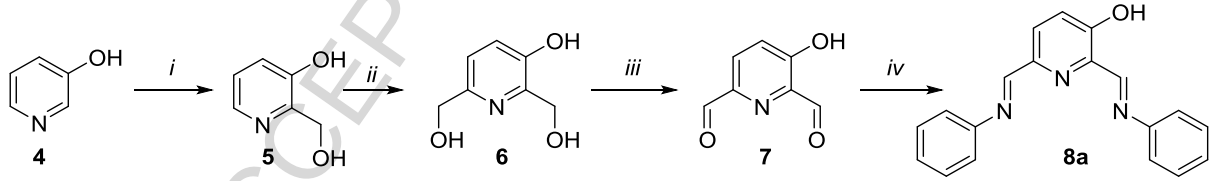


Scheme 1. Some examples of NN and NNN type complex

In this regard, we reported our own efforts towards achievement of these objectives by using ruthenium complexes coordinated with pyridinyl-based NNN ligand and investigated the catalytic behaviors in TH reactions. Complex **6a** bearing hydroxy substituent which is expected to be suitable for derivatization and immobilization has been found to display high catalytic activity in the TH reaction.

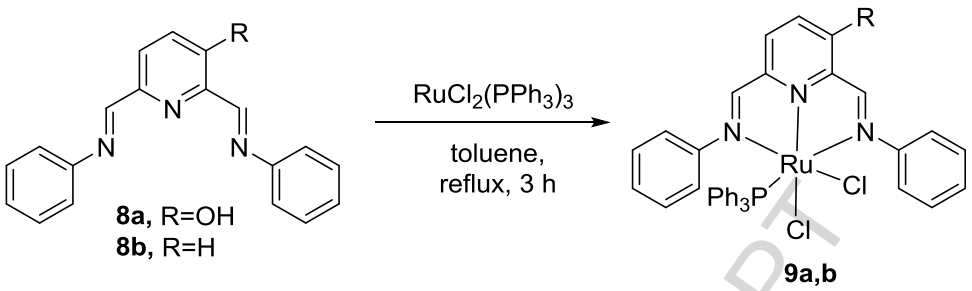
Results and Discussion

3-hydroxypyridine-2,6-dicarbaldehyde was prepared in a two-step reaction in accordance with the known procedure with a minor revision.[23] Firstly, 3-hydroxy pyridine **4** was converted to dicarbinol pyridine **6** by using excess amount of formaldehyde water solution in the reaction in order to eliminate the monocarbinol pyridine **5** and the residue was purified through column chromatography. Then, the dialcoholpyridine **6** was oxidized with SeO_2 in dioxane at reflux for overnight to afford pyridine dicarbaldehyde **7**. The imine **8a** was synthesized via condensation of dicarbaldehyde **7** and aniline in EtOH under reflux.



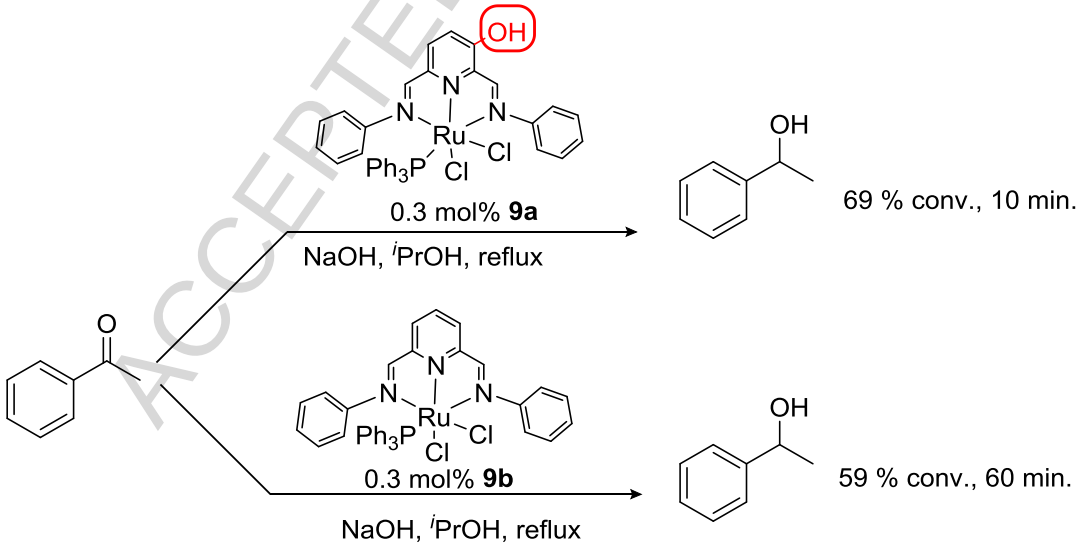
Scheme 2 Reagent and Conditions*: i-ii*: 4 mol equiv. formaldehyde, NaOH in EtOH, at 90 °C for 24 h, *iii*: SeO_2, dioxane, reflux, overnight, *iv*: 2.2 mol equiv. aniline in EtOH at reflux for 4 h.

The complexes **9a**,**b** were prepared with high yields via treatment of $RuCl_2(PPh_3)_3$ with ligand **8a,b** in degassed toluene at reflux temperature for 3 h under nitrogen (scheme 3). The complexes **9a,b** were characterized using NMR, HRMS, and FT-IR analyses. The signals for CH protons of imine in the complex **9a** were shifted upfield (at 7.76 and 7.74 ppm) with respect to the ligand **8a**. Besides, the signal at 36.84 ppm as a single peak in the ^{31}P NMR spectrum indicated the existence of the phosphorus moiety on the complex **9a** as well. While the complex **9a** was air and moisture stable, some decomposition was observed in complex **9b**.



Scheme 3. Preparation of complexes **9a,b**.

Yu and coworkers explained that the electron donating groups onto the coordinative imidazolyl arm of the ligand promoted the catalytic activity of the Ru(II) catalysts.[22] While obtaining a TOF value of 5820 h^{-1} from methyl substitued imidazoyl ring, unsubstituted ones showed a TOF = 3880 h^{-1}. In this respect, we assumed that the hydroxyl group on β-position of the pyridine ring of complex **9a** could have a similar accelerating effect onto the TH reaction. Therefore, we investigated this influence of complex **9a** by comparing the results in the absence of OH group as substituent on pyridine of complex **9b**. Initial tests were carried out in TH reaction of acetophenone by using the complexes **9a,b** in the presence of NaOH as a base in ^{i}PrOH at reflux. The complex **9a** was enhanced with 69% conversion in 10 min (TOF = 1380 h^{-1}), but the complex **9b** resulted in 59% conversion in 60 min (TOF = 196 h^{-1}) under the same reaction conditions (Scheme 4).



Scheme 4. The effect of substituent on the catalyst in the TH reaction

With the aim of obtaining reliable results, the full geometry optimizations for ground states of studied complexes **9a,b** were performed through the application density functional theory (DFT) calculations. The geometry optimized structures of **9a, 9b,** and **9c** are illustrated in Figure 1. One way to amplify the catalytic activity of the complex is to generate more active hydride species, which may be achieved through base activation.[24] Introduction of a base results in deprotonation of acidic groups, that is, OH in the present case. In order to determine whether base activation via deprotonation has any kind of influence on the activation of hydride in hydrogen transfer reaction, the NBO analysis has been performed for O(H) complexes. The NBO analysis examines all possible interactions between filled (donor)

Lewis-type NBOs and empty (acceptor) non-Lewis NBOs and estimates their energetic importance by second-order perturbation theory.[25] Natural (localized) orbitals are used to calculate distribution of the electron density in atoms and in bonds between atoms. The catalytic activity of the Ru complex has been influenced by the negative charge development on the hydrogen atom bonded to Ru. The larger negative charge absolutely on hydrogen is, the more powerful is hydride source the complex. The electronic properties of the complex at the metal center were modulated by deprotonation of OH group, providing a more electron rich hydride. The results of NBO analysis reveal that the positive charge on central Ru atom decreases together with an increase in negative charge development on hydrogen going from pyridinyl **9b** to pyridinyl oxide **9c**. Therefore, **9b** is expected to possess better catalytic activity.

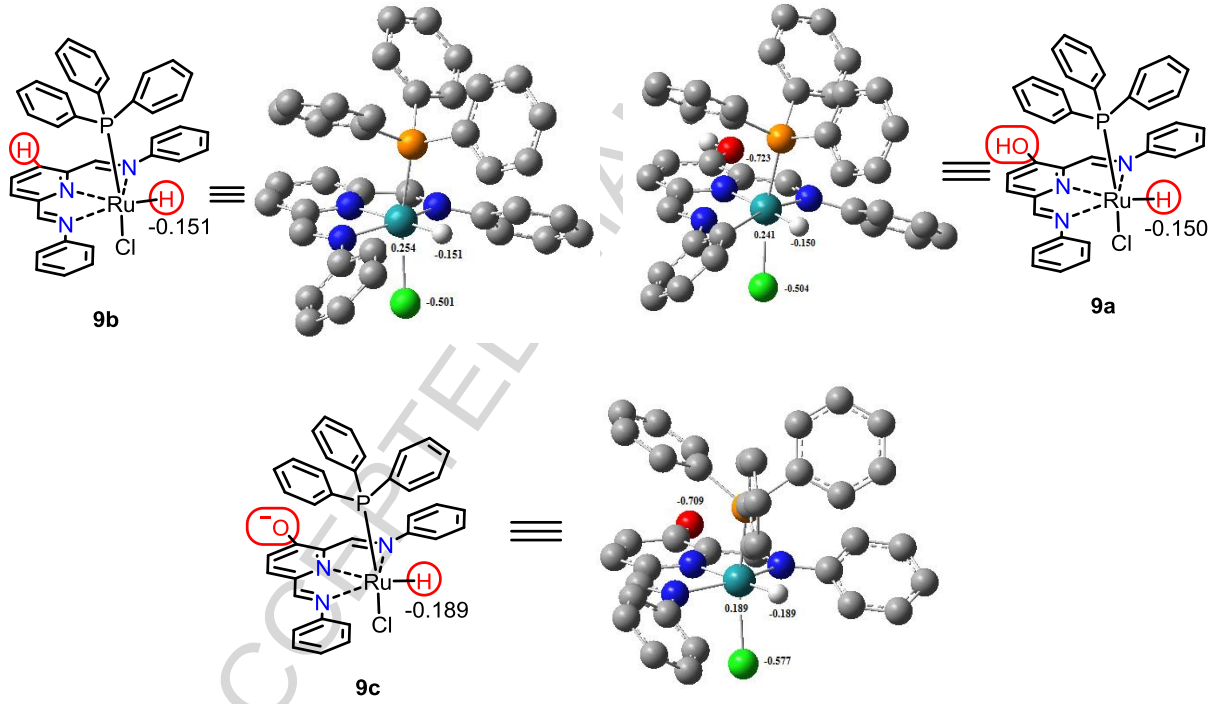


Figure 1. Geometry optimized structures of complexes and charges on central atoms. Hydrogens are deleted for clarity.

Several screenings were performed in order to determine the most convenient base and substrate-catalyst ratios. We began optimization reactions by screening the base (NaOH, KOH, NaO^{i}Pr, KO^{t}Bu and NaO^{t}Bu) with acetophenone as a model substrate in 10 min at reflux. As can be seen in Table 1, the best result was obtained in the presence of NaO^{i}Pr (entry 3). (Increasing the catalyst loading up to 5/1000 ratio slightly improved the conversion). The catalyst loading up to 5/1000 ratio to acetophenone increased the corresponding alcohol conversion (entries 6 and 7). Finally, rising the amount of base did not lead to any change in the previous result (entries 8 and 9).

Table 1. Optimization studies for complex **9a** in TH reaction of acetophenone

entry	C/S	base	time (min)	conv. %[a]
1	3/1000	NaOH	10 (60)	69 (90)

2	3/1000	KOH	10	58
3	3/1000	NaO^iPr	10	80
4	3/1000	NaO^tBu	10	63
5	3/1000	KO^tBu	10	56
6	4/1000	NaO^iPr	10	84
7	5/1000	NaO^iPr	10	93
8	5/1000	NaO^iPr^b	10	87
9	5/1000	NaO^iPr^c	10	77

Conditions: 0.003 mmol **9a**, 1 mmol acetophenone, 0.3 mL 0.1 M base, in 10 mL ^{i}PrOH, reflux, C/S: catalyst/substrate, [a]determined by GC, [b]0.5 mL, [c]0.8 mL.

Optimized condition in hand (0.3 mL 0.1M NaO^iPr as a base, 0.5 mmol % of catalyst **9a** and in 10 mL ^{i}PrOH at reflux), a series of aromatic and aliphatic ketones were explored in TH reaction and the related results are shown in Figures 2. In general, the reduction of acetyl group bearing aromatic substrates **10-23** proceeded with high conversions ranging between 84-97%. Interestingly, the *o*-methoxy substitute acetophenone **14** resulted in very low conversion (4%) in 2h. When methyl group of acetyl was displaced with isopropyl group **25**, relatively moderate conversion was obtained because of the steric hindrance. The similar result was also observed from the reduction of the tetralone **26** as well.

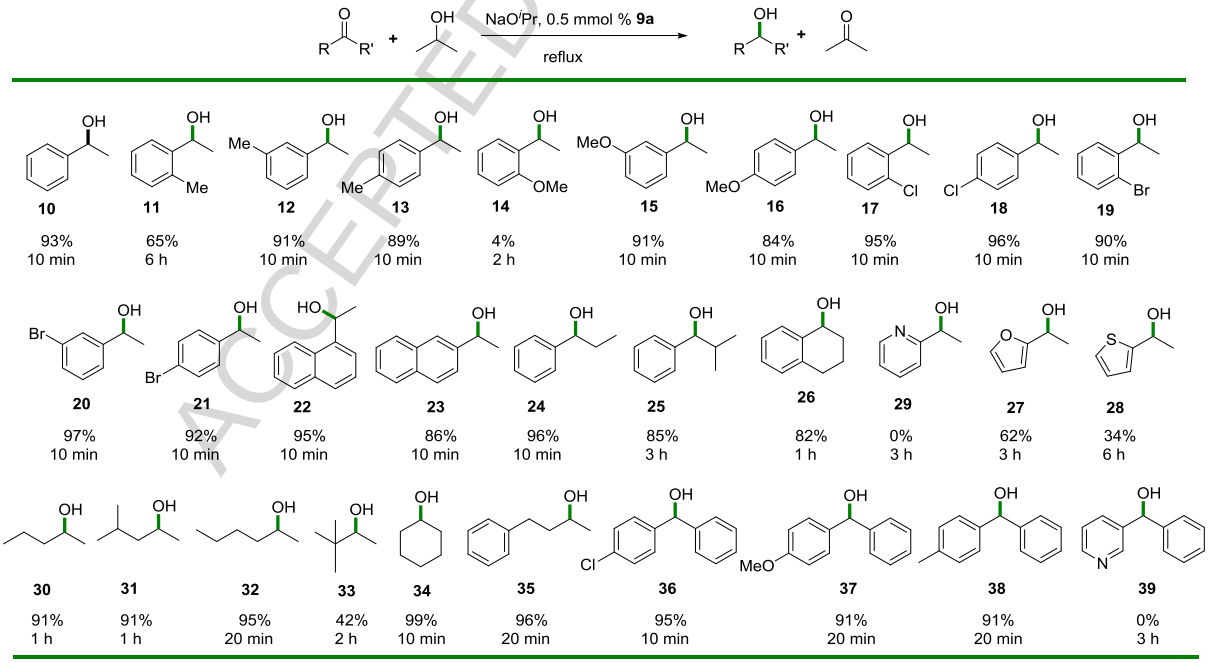


Figure 2. Transfer hydrogenation of ketones catalyzed by complex **9a**

In addition, we carried out the TH reaction of acetyl heteroaromatic ketones. The catalysis on the reaction rate diminished significantly from furyl **27** to thiophenyl **28** and it was realized that no product was observed from the reduction of acetyl pyridine **29**. So, we assumed that the presence of an extra chelating nitrogen atom could be coordinated with ruthenium and the reaction did not progress due to any kind of an interaction between catalyst and substrate. When a mixture of acetophenone and acetyl pyridine was used in the reaction condition, trace amount of acetophenone was obtained (less than 1% conversion) and also ^{31}P NMR spectrum

of acetyl pyridine and complex **9a** mixture supported this assumption as well (phosphorus signal was shifted to downfield from 36.84 to 39.07 ppm). The reduction of phenyl 3-pyridinyl ketone **39** displayed the similar result. Several aliphatic ketones **30**-**35** were also examined in TH reaction, which gave the corresponding secondary alcohols with high conversions. The catalyst displayed low reactivity in the reduction of sterically hindrance pinacolone **33**. In the case of the diaromatic ketones **36-38**, the catalyst demonstrated considerable activity.

Conclusion

In summary, we prepared novel NNN type pyridine based ruthenium (II) complexes and explored their use as catalysts for TH reaction of ketones. Due to the electronic effects, a significant difference was observed on the catalysis efficiency between the ruthenium complexes. Besides, the complex **9a** enabled potential solubility in a polar solvent by virtue of a hydroxyl group on β-position of the pyridine ring. Extended studies on the design and synthesis of transition metal complexes which are capable of preparing a heterogeneous catalyst by deposition on available commercial solid material linking with hydroxyl group are ongoing.

Acknowledgements

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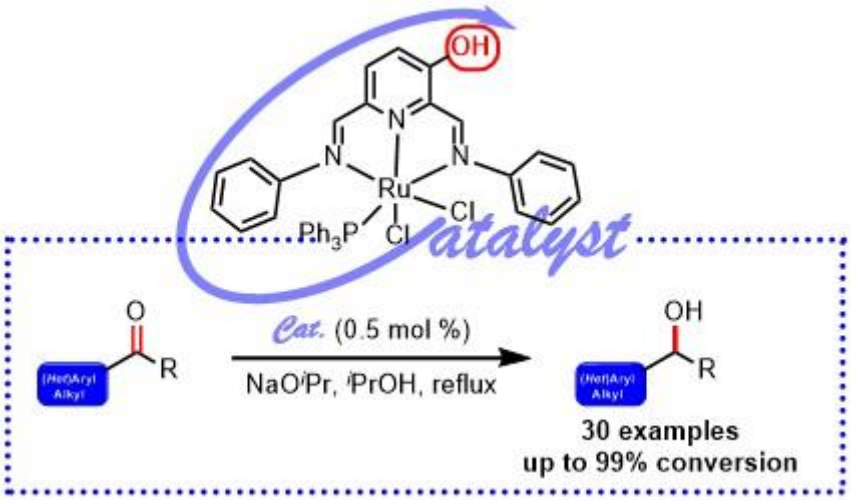

Graphical abstract

Highlights

- Easily prepared atom economic catalyst
- Hydroxyl group on the complex shows a dramatic effect on the catalyst efficiency
- Capable of preparing heterogeneous catalysts via immobilization on hydroxyl group